

Experience with Chlorine
Dioxide at Denver's Reuse Plant

Denver Water Dept., CO

Prepared for

Environmental Protection Agency, Cincinnati, OH

1986



U.S. Department of Commerce
National Technical Information Service

NTIS

TECHNICAL REPORT DATA

(Please read instructions on the reverse before completing)

PB87-115721

1. REPORT NO. EPA/600/J-86/148		3. RECIPIENT'S ACCESSION NO.	
4. TITLE AND SUBTITLE EXPERIENCE WITH CHLORINE DIOXIDE AT DENVER'S REUSE PLANT (Journal Version)		5. REPORT DATE 1986	
7. AUTHOR(S) W.C. Lauer, S.R. Lohman, and S.E. Rogers		6. PERFORMING ORGANIZATION CODE	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Denver Water Department, Denver, CO 80254		8. PERFORMING ORGANIZATION REPORT NO.	
12. SPONSORING AGENCY NAME AND ADDRESS Water Engineering Research Laboratory- Cincinnati, OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268		10. PROGRAM ELEMENT NO.	
		11. CONTRACT/GRANT NO. CS-806821	
		13. TYPE OF REPORT AND PERIOD COVERED Journal Article	
		14. SPONSORING AGENCY CODE EPA/600/14	
15. SUPPLEMENTARY NOTES Project Officer, John English J. American Water Works Association 78(6):79-87, June 1986			
16. ABSTRACT Researchers at Denver's reuse demonstration plant found that the effectiveness of chlorine dioxide treatment is critically dependent on the performance of the generator. Because high chlorine dioxide yields can be obtained even when excessive concentrations of undesirable by-products are present, chlorine dioxide yield alone cannot be used as a measure of optimum generation conditions. It is necessary to monitor carefully all of the various chlorine species produced--chlorite, chlorine, and chlorate, as well as chlorine dioxide.			
17. KEY WORDS AND DOCUMENT ANALYSIS			
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	
		c. COSATI Field/Group	
18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC		19. SECURITY CLASS (This Report) UNCLASSIFIED	
		20. SECURITY CLASS (This page) UNCLASSIFIED	
		21. NO. OF PAGES 11	
		22. PRICE	

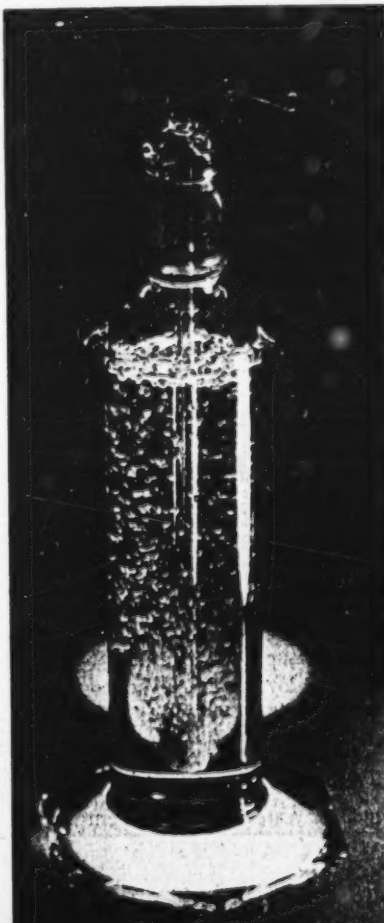
Experience With Chlorine Dioxide at Denver's Reuse Plant

William C. Lauer, Stephen R. Lohman, and Stephen E. Rogers

Researchers at Denver's reuse demonstration plant found that the effectiveness of chlorine dioxide treatment is critically dependent on the performance of the generator. Because high chlorine dioxide yields can be obtained even when excessive concentrations of undesirable by-products are present, chlorine dioxide yield alone cannot be used as a measure of optimum generation conditions. It is necessary to monitor carefully all of the various chlorine species produced—chlorite, chlorine, and chlorate, as well as chlorine dioxide.

The Denver (Colo.) Water Department's potable water reuse demonstration project was begun in 1979 following more than 10 years of pilot study. A 1-mgd (3.8-ML/d) treatment plant, which serves as the main test facility for studying the conversion of unchlorinated secondary wastewater effluent to potable water quality, was completed in fall 1985 at a cost of approximately \$18 million. Initial plant testing was begun in January 1984 and continued through the final stages of construction.¹ The demonstration plant processes (Figure 1) consist of lime clarification, recarbonation, filtration, ion exchange with ammonia removal and a regenerant recovery system, two-stage activated carbon adsorption with a thermal fluidized-bed regeneration furnace, an ozone system, reverse osmosis, air stripping, and chlorine dioxide disinfection. The project will cost \$29 million, \$7 million of which is being contributed by the US Environmental Protection Agency (USEPA), and includes a minimum of five years of operation, health effects testing, a comprehensive analytical studies program, as well as an intensive public information program.²

Chlorine dioxide is considered to be a more effective viricide and bactericide than chlorine and to reduce the potential for formation of chlorinated organics.



Project goals

A proposal for potable reuse raises many questions regarding safety, reliability, public acceptance, and technical and economic feasibility. The demonstration project addresses each of these questions and aims to³

- demonstrate the reliability of the process,
- prove product water safety,
- promote public education,
- generate regulatory agency acceptance, and
- provide the data necessary for large-scale implementation.

The demonstration plant is the physical heart of the project. Typically, such a plant might contain only the unit processes and associated equipment needed to address technical and economic feasibility. Denver's reuse demonstration plant encompasses these aspects, but also contains other elements that are specifically directed at each of the other project goals.

Multiple-barrier design

Drinking water supplies should be of the highest quality available.⁴ However, as traditional water resources become polluted by wastewater discharges or depleted, high quality sources may eventually become unavailable. Indirect reuse systems, currently being used to satisfy consumer demands, rely on unproven "natural" processes.⁵ Direct reuse requires redundancy and reliability in process design, known as the multiple safety barrier concept.^{6,7}

A multiple-barrier design consists of a series of unit processes to ensure that no single process bears the total burden for

W.C. LAUER ET AL. 79

removing any one toxic agent.⁸ At the reuse demonstration plant, several processes were selected that had multiple contaminant removal capabilities.⁹ For example, high-lime treatment was selected for phosphorus and heavy metal removal.⁵ But this process is also effective in removing suspended solids and total organic carbon, in addition to inactivating viruses and bacteria.^{10,11} Multiple barriers for pathogen removal consist of high-lime treatment, ozonation, reverse osmosis, as well as chlorine dioxide disinfection.

Process selection

Because of the untested nature of potable reuse technology, it was determined that any process involved must be demonstrated on a plant scale prior to actual application. In December 1974, the Denver Water Department hosted a seminar to combine the knowledge of various consulting engineers and prominent technical experts associated with universities and state and federal agencies with that of its own staff and co-workers at the University of Colorado. The idea of the seminar was to design, in concept, a process capable of reliably and consistently treating wastewater to produce high quality water safe for human consumption.¹² Although the recommended treatment scheme did not represent a unanimous consensus, it did represent a consolidated opinion.

In early 1975, the Denver Water Department charged a consulting firm* with developing a preliminary design⁵ for a potable reuse demonstration plant based on the firm's knowledge and on the advice and opinions presented in the seminar. The resulting design was revised following meetings with the USEPA in 1979 and further pilot studies with the University of Colorado. The unit processes selected can be grouped into six removal or control operations:¹³ phosphorous removal, suspended solids removal, nitrogen removal, soluble organic removal, dissolved salts removal, and disinfection.

For each of these operations, there are one or more unit processes capable of achieving the desired result. Since the initial process selections in 1975, advances in technology and operating experience at pilot- and full-scale facilities have provided data on each of these control processes. The selection of a specific unit process was made on the basis of the required removal efficiencies and the various side benefits provided, i.e., removal of other constituents. The selection was also based on the operating history and probable success of the unit process and on the operating difficulty or operating constraints associated with each. The rationale for selecting the unit

*CH2M Hill, Denver, Colo.



Because chlorine dioxide cannot be stored, it is generated on-site and pumped immediately to the water.

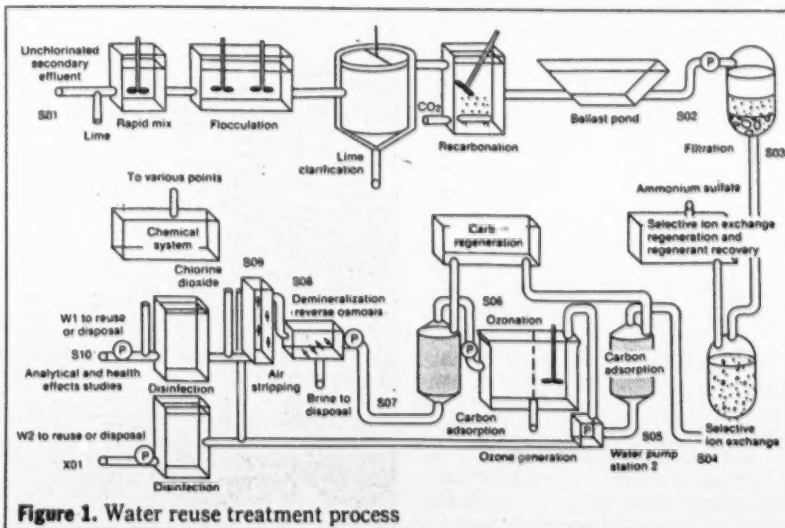
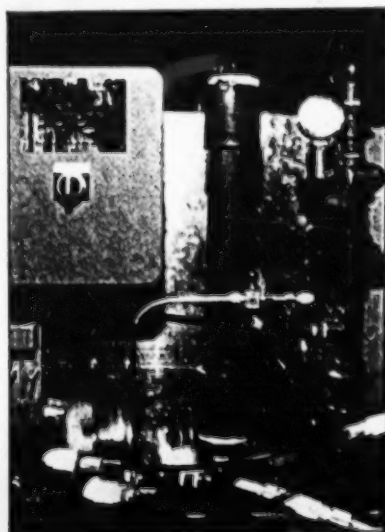
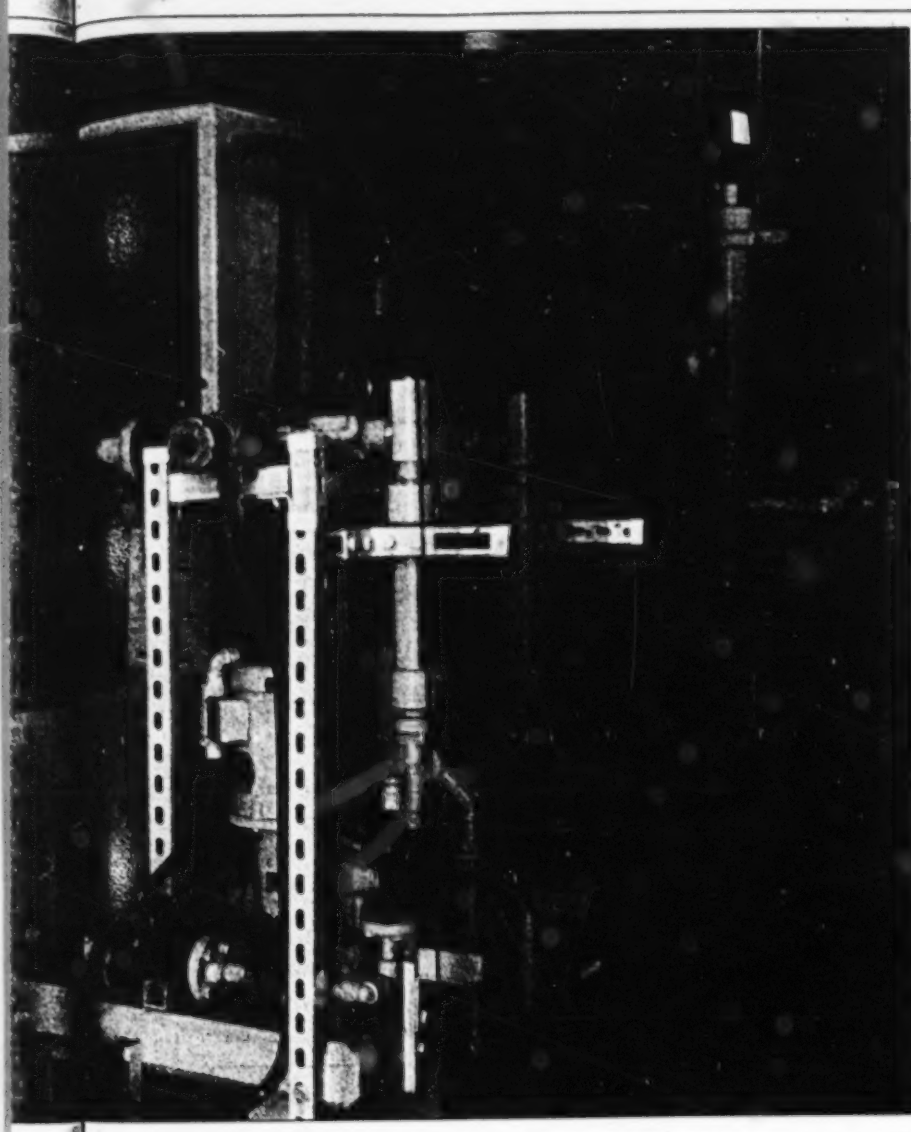


Figure 1. Water reuse treatment process



processes for each removal category has been discussed elsewhere.¹³

Disinfection

Engendering public confidence in the potable reuse of reclaimed domestic wastewater is a major objective of the demonstration project,¹² for without that confidence implementation of the full-scale direct reuse facility is doubtful. Because disease-causing organisms represent the most acute hazard to the public, the production of a water free of pathogenic organisms is paramount to the success of the project. The methods of disinfection available involve the use of strong oxidants and include chlorine (Cl_2), ozone (O_3), ultraviolet irradiation (UV), and chlorine dioxide (ClO_2).

Three chlorine dioxide generation systems were evaluated at Denver.

Chlorine. The advantages of Cl_2 as a disinfectant are its ease of application and the detailed information available concerning its use. Many studies have indicated the various contact times and disinfectant dosages that are effective against such organisms as indicator bacteria, viruses, and cysts. The disadvantages of Cl_2 are the by-products formed when it reacts with various organic precursors.

Ozone. Ozone is a very strong oxidant and has shown to be effective against bacteria, viruses, and cysts. In potable reuse pilot studies, Schmaus¹⁴ found nearly complete removals of total coliforms when 15 mg O_3/L was applied for contact periods of 6 min and similar removals with 10 mg O_3/L and 10 min of contact. Questions concerning the formation of oxidation by-products (e.g., epoxides) with O_3 are currently under investigation.

Ultraviolet irradiation. The problems associated with UV disinfection involve the passage of the light through water. Relatively clear solutions are necessary to ensure proper disinfection, and the design of the UV system must be such that the water passes over the UV source in thin sheets. For large plants, these design constraints can cause severe problems.

Chlorine dioxide. Chlorine dioxide has been favored as a disinfectant in the last few years, and the USEPA has conducted several studies¹⁵ utilizing the compound to disinfect water and wastewater. It has been reported¹⁶⁻¹⁸ that ClO_2 is a more efficient viricide and bactericide than chlorine and is effective over a wide pH range.¹⁶ The careful control of ClO_2 disinfection reduces the potential for formation of chlorinated organics.¹⁹ Chlorine dioxide must be generated on-site and is usually the product of the reaction of Cl_2 gas with sodium chlorite (NaClO_2). Because of the extremely rapid kinetics of ClO_2 reactions, it is necessary to disperse the ClO_2 into the water quickly to provide intimate contact for complete disinfection.

Chlorine was originally chosen as the disinfectant for the demonstration plant, but because of concern over chlorinated organics and oxidative by-products, the disinfection process was changed to ClO_2 . Because the feedwater for the demonstration plant is unchlorinated secondary wastewater effluent, there is no Cl_2 at any point in the system.

Demonstration plant operation

The reuse plant, with a limited set of processes, became operational in January 1984. Startup operations have previously been reported by Rogers and Lauer.¹⁰ Processes were phased in until February 1985, when the reverse osmosis system became operational. Because of construction-related delays, many of the processes

were not consistently or reliably operated, but all of the disinfection unit processes, including ClO_2 , were fully operational, albeit in a startup configuration. The final critical construction components were completed by fall 1985. Phase 1 testing²⁰ began on October 1 with the implementation of the routine analytical studies program and with the following process in continuous operation: lime clarification (pH 11.2), recarbonation (pH 7.8), multimedia pressure filtration, activated carbon adsorption (30-min empty bed contact time [EBCT]), ozonation, activated carbon adsorption (30-min EBCT), reverse osmosis, air stripping, and ClO_2 disinfection.

Chlorine dioxide generators

Chlorine dioxide is generated by reacting an acidified Cl_2 solution (pH 2-3) with NaClO_2 to produce a ClO_2 solution, which is then metered (pumped) to the final product water (W1, sample point S10, Figure 1) and the intermediate process water (W2, sample point X01, Figure 1). Intermediate process water is used for landscape irrigation and for backwash of filters, ion exchange columns, and first-stage activated carbon adsorption. Chlorine dioxide can also be supplied in large doses to the filters, ion exchange columns, first- and second-stage activated carbon, as well as the air-stripping column for shock treatment of these processes. A schematic of the feed system is provided in Figure 2.

Three different ClO_2 generation systems have been utilized thus far. The main features of the first system, which was the design system provided under the original construction contract, were a NaClO_2 feed pump capacity of 19 gph (72 L/h), and a ClO_2 output of 17-170 lb/d (7.7-77.1 kg/d).

After the design, system had been operated for a short period, it became obvious that the system was oversized to the point that it could not be controlled. The NaClO_2 feed pumps, for example, were at least 50 times too large. This necessitated pump speed and stroke settings of 1 percent to achieve the desired delivery, even when the NaClO_2 solution was diluted. The pumps could not operate consistently at these settings. Because the entire system was similarly oversized and would have required complete rebuilding to operate properly, it was abandoned.

A self-contained system (Figure 3) replaced the design system. The principal features of the system, which was housed in a 3-ft $\times$ 3-ft (0.9-m $\times$ 0.9-m) fiberglass enclosure, were a NaClO_2 feed pump capacity of 0.05-0.26 gph (0.18-0.98 L/h), and a chlorine dioxide output of 2.4-12.5 lb/d (1.0-5.6 kg/d).

This system was operated for more than a year, and most of the data obtained thus far reflect the operation of this

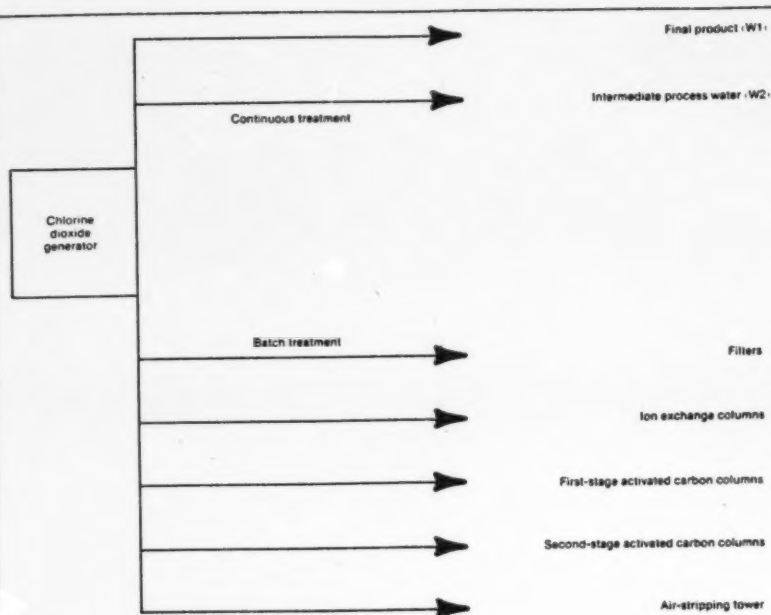


Figure 2. Schematic of chlorine dioxide feed system

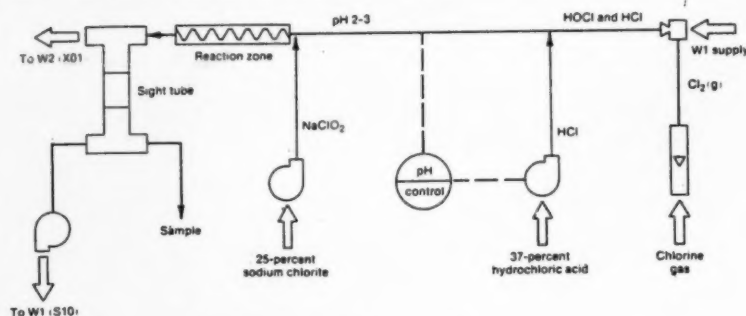


Figure 3. Schematic of chlorine dioxide generator 2

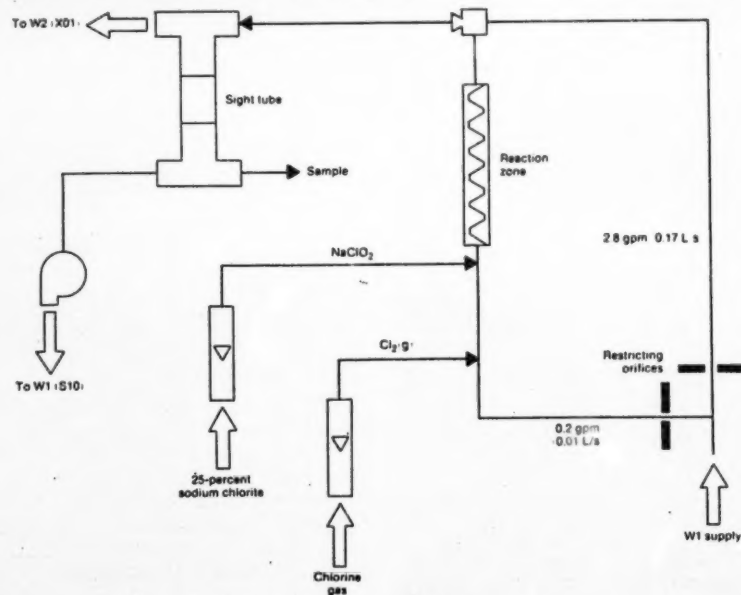


Figure 4. Schematic of chlorine dioxide generator 3

were not consistently or reliably operated, but all of the disinfection unit processes, including ClO_2 , were fully operational, albeit in a startup configuration. The final critical construction components were completed by fall 1985. Phase 1 testing²⁰ began on October 1 with the implementation of the routine analytical studies program and with the following processes in continuous operation: lime clarification (pH 11.2), recarbonation (pH 7.8), multimedia pressure filtration, activated carbon adsorption (30-min empty bed contact time [EBCT]), ozonation, activated carbon adsorption (30-min EBCT), reverse osmosis, air stripping, and ClO_2 disinfection.

Chlorine dioxide generators

Chlorine dioxide is generated by reacting an acidified Cl_2 solution (pH 2-3) with NaClO_2 to produce a ClO_2 solution, which is then metered (pumped) to the final product water (W1, sample point S10, Figure 1) and the intermediate process water (W2, sample point X01, Figure 1). Intermediate process water is used for landscape irrigation and for backwash of filters, ion exchange columns, and first-stage activated carbon adsorption. Chlorine dioxide can also be supplied in large doses to the filters, ion exchange columns, first- and second-stage activated carbon, as well as the air-stripping column for shock treatment of these processes. A schematic of the feed system is provided in Figure 2.

Three different ClO_2 generation systems have been utilized thus far. The main features of the first system, which was the design system provided under the original construction contract, were a NaClO_2 feed pump capacity of 19 gph (72 L/h), and a ClO_2 output of 17-170 lb/d (7.7-77.1 kg/d).

After the design, system had been operated for a short period, it became obvious that the system was oversized to the point that it could not be controlled. The NaClO_2 feed pumps, for example, were at least 50 times too large. This necessitated pump speed and stroke settings of 1 percent to achieve the desired delivery, even when the NaClO_2 solution was diluted. The pumps could not operate consistently at these settings. Because the entire system was similarly oversized and would have required complete rebuilding to operate properly, it was abandoned.

A self-contained system (Figure 3) replaced the design system. The principal features of the system, which was housed in a 3-ft $\times$ 3-ft (0.9-m $\times$ 0.9-m) fiberglass enclosure, were a NaClO_2 feed pump capacity of 0.05-0.26 gph (0.18-0.98 L/h), and a chlorine dioxide output of 2.4-12.5 lb/d (1.0-5.6 kg/d).

This system was operated for more than a year, and most of the data obtained thus far reflect the operation of this

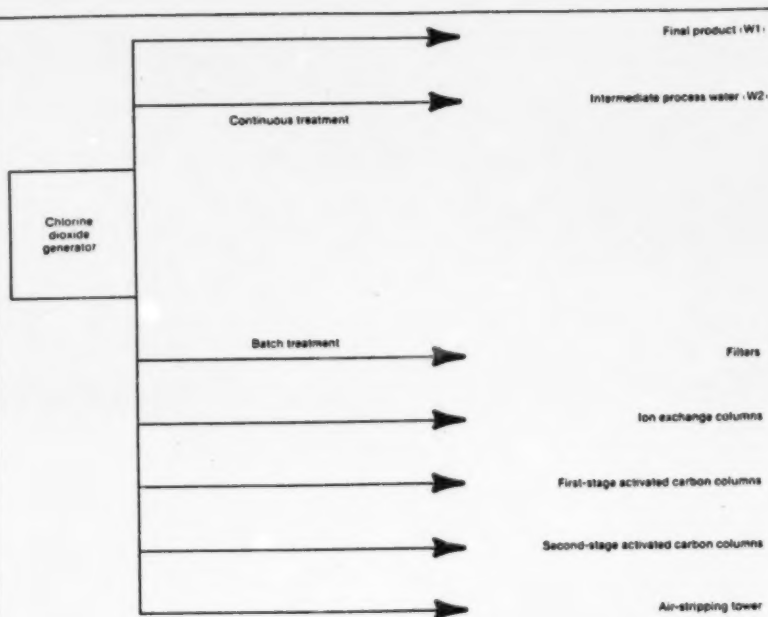


Figure 2. Schematic of chlorine dioxide feed system

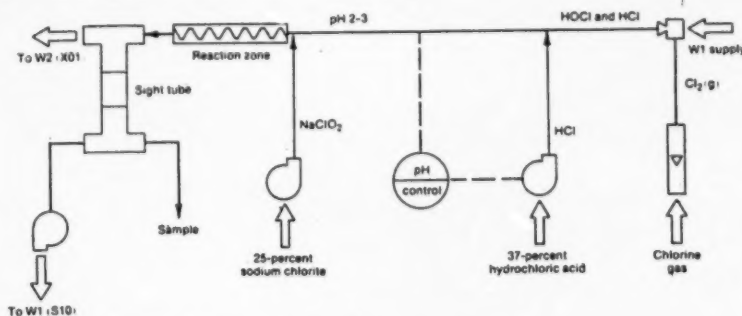


Figure 3. Schematic of chlorine dioxide generator 2

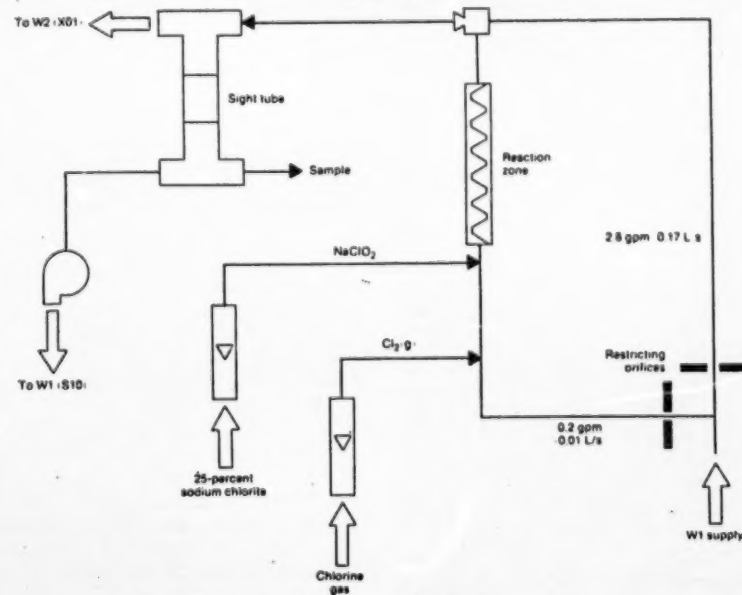


Figure 4. Schematic of chlorine dioxide generator 3

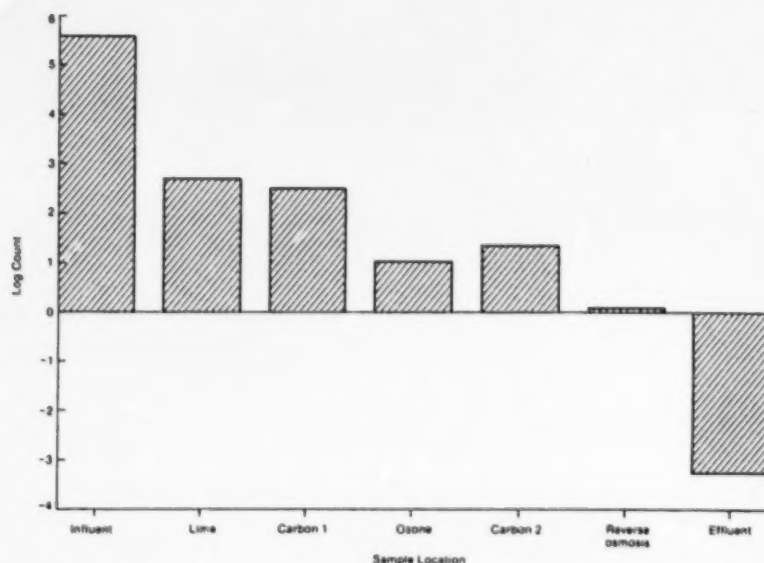


Figure 5. Mean total coliform counts (per 100 mL) throughout the treatment plant (Mar. 1–Nov. 1, 1985)

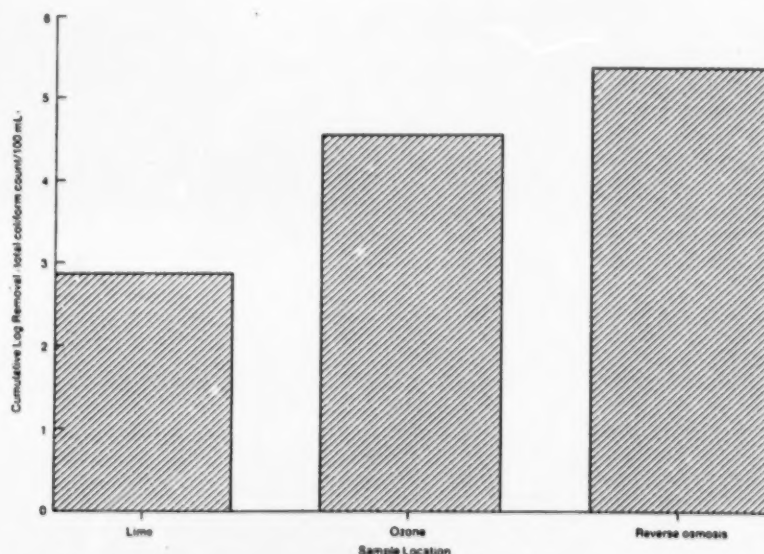


Figure 6. Cumulative log removal of coliforms throughout the treatment plant (Mar. 1–Nov. 1, 1985)

generation configuration. Although this system was far superior to the design system, inconsistent feed, resulting primarily from the characteristics of the NaClO_2 pump, was a serious problem. After months of failure to stabilize the system, a new generator was installed in November 1985.

This third system operates on a vacuum principle to deliver the reactants and should be capable of optimum performance. Although the unit has been in operation only a relatively short time, special studies were initiated to compare performance data. The system (Figure 4) incorporates a sodium chlorite feed rate of 0.12–0.89 gph (0.45–3.36 L/h) and a chlorine dioxide output of 5.8–41.8 lb/d (2.6–18.9 kg/d).

Generator performance

Chlorine dioxide treatment is critically dependent on the performance of the generator. Because high ClO_2 yields can be obtained even when excessive concentrations of undesirable by-products, e.g., chlorite, chlorate, are present,²¹ measurements of ClO_2 yields alone cannot be relied upon to ensure optimum generation conditions. The numerous competing reactions that may take place depend not only on the concentrations of the reacting species but also on pH, temperature, reaction time, and mixing characteristics. It is necessary to monitor carefully the various chlorine species produced in order to optimize generator performance. The primary chlorine species of interest are ClO_2 , chlorite (ClO_2^-), Cl_2 , and chlorate (ClO_3^-). Tests for these chlorine species are very time consuming (entailing one hour per test set) and require a trained analyst to produce reliable results.

Absorbance at 440 nm can be used to measure the ClO_2 content, i.e., yield, of generator solutions, without the need to dilute the sample if interferences are not present.²² This method is useful for repeated operator monitoring of the stability of the generation system and for determining the ClO_2 output. It must be emphasized, however, that speciation tests²¹ must be performed and correlated with the ClO_2 absorbance results to ensure that undesirable species are within acceptable levels. Standard operating procedures at the reuse plant are twice-daily ClO_2 yield tests supported by weekly speciation analyses.

Two generators have undergone the type of evaluation just described. The first system (generator 2) utilized pumped NaClO_2 and educted Cl_2 solution, with a water flow in the generator mixing zone of about 1.5 gpm (0.09 L/s). A second system (generator 3) educted both NaClO_2 and Cl_2 solution into the reaction mixing zone before it was mixed with the eductor water (2.8 gpm [0.17 L/s]).

TABLE 1
Results of speciation testing of generator 2

Run	NaClO ₂ Feed mL/min	Cl ₂ Feed		Generator Concentration—mg/L				Calculated Yield percent	Unreacted ClO ₂ ⁻ percent	Excess Cl ₂ percent
		lb/d	kg/d	ClO ₂	Cl ₂	ClO ₂ ⁻	ClO ₃ ⁻			
1	13.2	8.0	3.6	465	131	*	11.1	98.1	0	52.6
2	13.8	7.3	3.3	465	120.5	11.8	33.4	92.3	2.3	45.5
3	15.5	9.8	4.4	681	159	13.5	*	98.1	1.9	43.6
4	15.5	9.8	4.4	651	170	6.8	*	99.0	1.0	49.2
5	15.5	8.5	3.8	678	*	*	17.1	98.0	0	0
6	15.5	7.5	3.4	627	57	3.4	34.3	95.3	0.5	16.5
7	26.2	13.2	5.9	903	120.5	13.5	85.3	91.6	1.0	23.3
8	25.7	12.7	5.7	1338.8	*	6.7	*	99.5	0.5	0
9	25.8	12.7	5.7	1011.7	85.1	6.7	*	99.3	0.7	15.9
10	26.0	12.5	5.6	984.8	106.4	23.6	143.7	87.6	2.1	18.0
11	26.0	12.5	5.6	548.4	335.7	8.1	381.1	63.4	0.7	73.9
12	17.3	8.7	3.9	537.9	135.6	1.7	*	99.7	0.3	47.8
13	11.0	6.7	3.0	396	114	21.9	*	94.8	5.2	51.9
14	11.0	6.7	3.0	428	125.8	13.5	54.2	88.2	2.8	49.3

*None detected

TABLE 2
Results of speciation testing of generator 3

Run	NaClO ₂ Feed mL/min	Cl ₂ Feed		Generator Concentration—mg/L				Calculated Yield percent	Unreacted ClO ₂ ⁻ percent	Excess Cl ₂ percent
		lb/d	kg/d	ClO ₂	Cl ₂	ClO ₂ ⁻	ClO ₃ ⁻			
1	24.5	13.6	6.1	575.7	30.7	4.4	63.0	91.2	0.7	9.3
2	24.5	12.5	5.6	587.1	19.1	6.7	41.7	93.6	1.0	5.8
3	24.5	10.2	4.6	522.7	3.9	30.4	46.4	88.5	5.1	1.3
4	25.0	9.9	4.4	516.0	*	20.2	62.2	88.0	3.4	*
5	24.0	11.6	5.2	465.0	*	*	69.5	89.2	*	*
6	13.8	11.0	4.9	357.5	138.2	*	13.9	97.0	*	71.4
7	13.82	5.8	2.6	308.6	4.4	10.1	33.4	89.3	2.9	2.4
8	9.06	4.7	2.1	222.6	*	*	41.7	86.9	*	*
9	9.06	5.1	2.3	209.1	3.5	*	13.9	94.9	*	3.0
10	8.42	5.0	2.2	205.7	12.1	*	18.0	93.4	*	10.5
11	8.42	5.7	2.5	170.3	30.4	*	29.2	87.8	*	29.9
12	8.0	4.3	1.9	181.8	44.8	2.0	25.6	88.0	1.0	41.3
13	8.1	4.2	1.9	198.3	37.6	0.7	13.9	94.3	0.3	34.1
14	8.8	4.0	1.8	188.9	*	*	41.7	84.9	*	*
15	7.85	4.3	1.9	195.6	3.5	*	26.4	90.2	*	3.1
16	8.5	4.3	1.9	232.7	12.9	*	19.5	93.6	*	9.9
17	8.5	4.3	1.9	233.4	13.5	*	23.0	92.6	*	10.2
18	8.5	4.3	1.9	244.2	20.6	*	23.0	92.9	*	14.9

*Not detected

TABLE 3
Results of microbiological testing (Mar. 1–Nov. 1, 1985)*

Microorganism	Sample Location										
	Raw Water (S01)	Lime (S02)	Filters (S03)	Carbon 1 (S05)	W2 (X01)	Ozone (S06)	Carbon 2 (S07)	Reverse Osmosis (S08)	Air Stripper (S09)	W1 (S10)	Denver Tap Water (S12)
Total coliforms—count/100 mL	3.82 × 10 ⁵	501.31	399.45	322.87	0.055	10.59	23.02	1.21	1.77	5.59 × 10 ⁻⁴	7.87 × 10 ⁻⁴
Log count	5.58	2.70	2.60	2.51	-1.26	1.02	1.36	0.08	0.25	-3.25	-3.10
m-HPC—count/mL	2.41 × 10 ⁵	2.48 × 10 ⁵	1.43 × 10 ⁵	1.14 × 10 ⁵	6.42	5.27 × 10 ⁴	6.46 × 10 ⁴	65.40	50.67	0.302	0.498
Log count	5.38	5.39	5.16	5.06	0.81	4.72	4.81	1.82	1.70	-0.52	-0.30
E. coli B—pfu/100 mL	2.14 × 10 ⁴	10.25	13.76	8.15		0.109	0.141	ND†	ND	ND	ND
Log count	4.33	1.01	1.14	0.91		-0.96	-0.85	ND	ND	ND	ND
E. coli C 3000—pfu/100 mL	3.88 × 10 ⁴	7.58	9.80	5.69		2.82 × 10 ⁻⁴	3.46 × 10 ⁻⁴	ND	ND	ND	ND
Log count	4.59	0.88	0.99	0.76		-3.55	-3.46	ND	ND	ND	ND
Fecal coliforms—count/100 mL	1.01 × 10 ⁴										
Log count	4.00									ND	ND
Fecal streptococci—count/100 mL	3.13 × 10 ³									ND	ND
Log count	3.50									ND	ND

*Geometric means and log geometric means

†ND—None detected

Results of speciation testing of generator 2 under a variety of conditions are listed in Table 1. Average ClO_2 yields of 465 mg/L, 659 mg/L, and 957 mg/L are represented by runs 1-2, 3-6, and 7-11, respectively. High excess Cl_2 concentrations were generally used to "drive" the reaction to produce high yields.²³ Although high yields of chlorine dioxide could be obtained, reactant concentrations or by-product values (or both) were often a concern. In runs 7-11, the generator was evaluated after initial settings were made with no further adjustments. Reactant feed data showed what appeared to be minor variations, although the generator speciation data fluctuated radically. Run 8 demonstrated that high yields with minimal by-product levels were obtainable, but elusive, with this generator system. Although numerous modifications were investigated, this inherent instability of the system could not be eliminated. With the exception of run 11, the fluctuations in performance would most likely not be detected by ClO_2 yield analysis alone. With the realization that the generator system design was responsible for the observed control problems, a new generator system was installed.

Generator 3 features the introduction of reactants to the mixing zone by eduction with a minimal water flow (0.2 gpm [0.01 L/s]), which has the advantage of maintaining high concentrations of Cl_2 and NaClO_2 for optimum reaction conditions.²³ Speciation results for several reaction variations are listed in Table 2. The generator is capable of producing high yields at lower concentrations of ClO_2 than generator 2. At concentrations below 1000 mg/L, generator 2 was not able to produce high yields without excess chlorine. Generator 3 has thus far produced ClO_2 yields of 90 percent with minimal excess Cl_2 at concentrations as low as 190 mg/L.

The speciation results for generator 3 indicate a sensitivity to changes in the NaClO_2 and Cl_2 feeds. However, compared with data from generator 2, the results are more consistent and predictable with respect to these changes. The results of runs 16-18, which examined generator performance without further adjustments, showed a marked improvement in stability compared with generator 2. Although various modifications and adjustments were made to generator 3, the lowest result obtained for ClO_3^- was 13.9 mg/L. This appears to be an inherent characteristic of this system. The pH of generator solution samples taken downstream of the reaction mixing zone ranged between 3 and 4. This is indirect evidence that the pH of the generator reaction zone may be above the optimum range of 2-3.¹⁹ Although this problem is yet to be fully resolved, the design of generator 3 has proved to

be superior to that of generator 2 in stability and in its capability to perform at lower concentrations.

Results of chlorine dioxide disinfection

Chlorine dioxide is used to disinfect process water at two sites in the treatment plant. Following first-stage activated carbon adsorption, the process stream is split. Nine tenths of the flow is disinfected with ClO_2 (location X01) and then used for irrigation and for backwashing filters, ion exchange columns, and first-stage activated carbon adsorption. One tenth of the flow (0.1 mgd [0.375 ML/d]) is treated by the remaining processes (ozone, second-stage activated carbon adsorption, reverse osmosis, and air stripping) prior to ClO_2 disinfection (location S10). These two feed points

provide a comparison of the effectiveness of chlorine dioxide for differing water qualities: (1) carbon-treated wastewater with high bacterial contamination and (2) a high purity water with extremely low bacterial populations.

Results of microbiological tests conducted at several locations in the plant are listed in Table 3. The sample locations (S01-S10) can be found in Figure 1. Denver tap water, location S12, is provided as a comparison standard. Fecal coliform²⁴ and fecal streptococcus²⁴ results represent a very limited data base. Coliphage test results¹¹ are listed as *E. coli* B and *E. coli* C (*E. coli* C 3000).

Profiles of the mean total coliform count²⁴ and mean membrane heterotrophic plate count (m-HPC)²⁴ through the treatment plant are shown in Figures

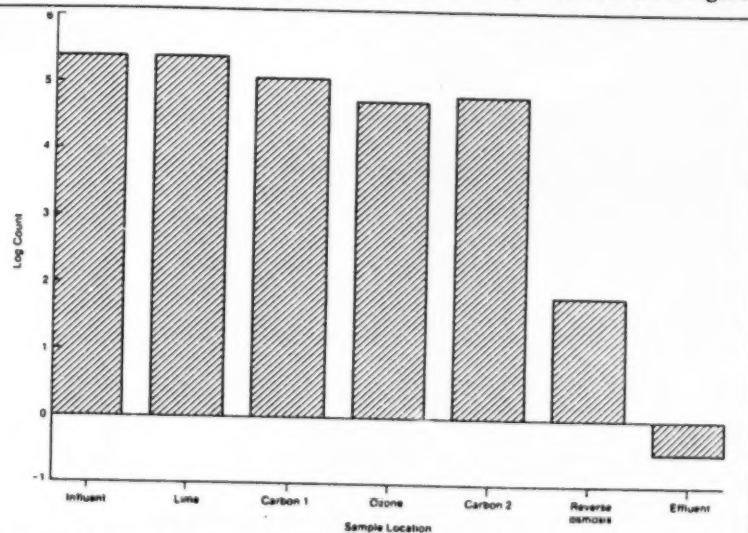


Figure 7. Mean m-HPC counts (per millilitre) throughout the treatment plant (Mar. 1-Nov. 1, 1985)

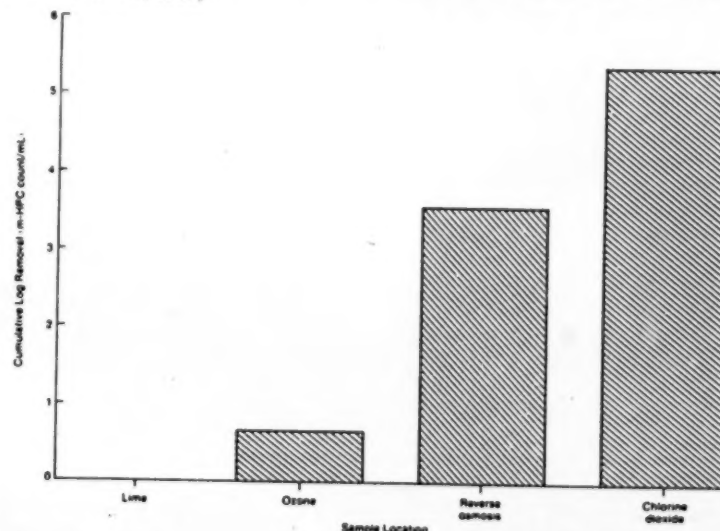


Figure 8. Cumulative log removal of m-HPC bacteria throughout the treatment plant (Mar. 1-Nov. 1, 1985)

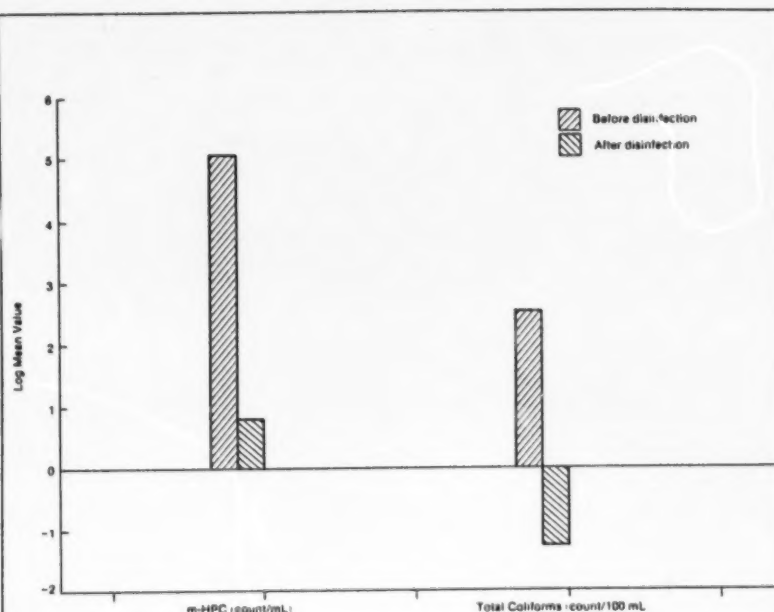


Figure 9. Chlorine dioxide disinfection of intermediate process water

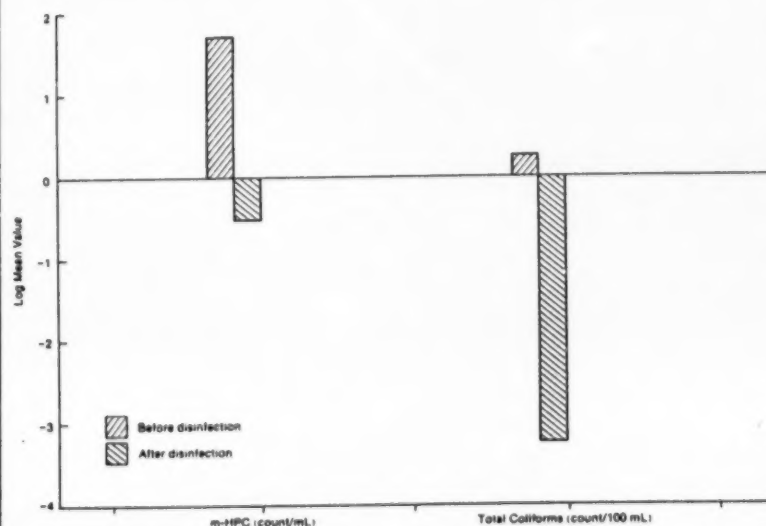


Figure 10. Chlorine dioxide disinfection of final product water

TABLE 4
Typical chemical analysis (Oct. 1-Dec. 1, 1985)

Parameter	Geometric Mean Value	
	Carbon Treated Water (X01)	Fully Treated Water (S10)
pH	7.5	6.1
Total organic carbon—mg/L	1.4	<0.1
Turbidity— <i>tu</i>	0.18	0.04
Hardness—mg CaCO ₃ /L	174.9	4.0
Total alkalinity—mg CaCO ₃ /L	217.5	4.0
Ammonia—mg/L as N	21.2	2.5
Dissolved oxygen—mg/L	1.4	7.6
Specific conductance— μ mhos/cm	859	50
Total dissolved solids—mg/L		9.7

5-8. Coliforms are reduced significantly by lime at a pH >11. Ozone further reduces the viable population to a low value. Following reverse osmosis, essentially no coliforms remain (Figure 6). Chlorine dioxide provides protection from regrowth.

Plate count organisms (m-HPC) react to the treatment processes somewhat differently. Lime treatment at a pH >11 has little effect on reducing the m-HPC count. Ozone reduces the numbers by less than one log (Figure 7). Reverse osmosis should form a physical barrier to bacteria, allowing essentially none to pass (Figure 8). However, although this process has a significant effect (more than three-log removal), some organisms have survived reverse osmosis treatment. Chlorine dioxide has been very effective in inactivating these bacteria almost completely (Figure 8). Leakage of bacteria past the reverse osmosis modules was the first indication that a problem existed with the integrity of the system. Conductivities and other measurements normally thought to indicate a failure of the membranes were all nominal. During an investigation, hair-line fractures were discovered in the product tubes that interconnect membrane modules. Replacement of these modules reduced bacterial counts following reverse osmosis. All of the membrane modules are now being carefully examined, and defective units are being replaced. The performance of the system with respect to bacterial rejection is expected to improve following this action.

Figures 9 and 10 show the results of ClO₂ disinfection at two locations for total coliform and m-HPC organisms. A four-log reduction in m-HPC values is observed at the intermediate treatment location (X01). After complete treatment and ClO₂ disinfection, mean m-HPC values are <1 count/mL. As already mentioned, total coliform results indicated that the disinfectant is being utilized primarily for extra insurance at the fully treated location (S10), whereas its disinfecting qualities are more apparent when it is used at the somewhat contaminated intermediate location (X01). When challenged with a nearly two-log total coliform count, the ClO₂ reduces the concentration to near zero. The excellent results shown in Figures 9 and 10 were obtained for locations X01 and S10, respectively, with minimal detention time (1.8 min, 3.8 min), low applied dosage (1.25 mg/L, 0.25 mg/L), minimal ClO₂ (0.9 mg/L, none detected), no ClO₃⁻ by-product, and no free or total Cl₂ residual detectable in the water. These results are extraordinary when compared with those obtained with free Cl₂, which, when applied at similar doses of 1.12 mg/L at X01 and 0.50 mg/L at S10, resulted in m-HPC values that were 40

times higher (240 count/mL) at X01 and 6 times higher (2.6 count/mL) at S10.

Table 4 lists typical results of chemical tests performed on the intermediate process water (X01) and the fully treated final plant effluent (S10). The X01 water resembles many drinking water supplies in its chemical composition, whereas the S10 sample resembles deionized water.

Chlorine dioxide has been used to "shock treat" various process components that became colonized by excessive bacterial populations. One example of this application is the disinfection of the filter media. During the early testing of the plant, it was observed that dissolved oxygen (DO) was being consumed across the filters. This phenomenon was somewhat mystifying in that the influent DO concentration was being elevated to near saturation by an air diffuser system installed in the ballast pond just prior to filter pumping. After passing through the filters (with only minimal contact time), the DO was reduced to approximately 2 mg/L. Activated carbon adsorption follows, and it is desirable to keep the entire column aerobic to study the adsorption characteristics. With such a low influent DO, this condition could not be assured. After investigation, it was confirmed that heavy bacterial colonization in the filters was responsible for the observed DO reduction. The columns were treated with high doses of ClO_2 (25–100 mg/L) for various lengths of time (2–6 h). A 50-mg/L dose for 2 h was found to be optimum. Following this treatment, there was no measurable DO loss across the filters. This treatment has been repeated whenever necessary—about every three months.

Summary

Chlorine dioxide has been shown to be an effective disinfectant for bacterial indicators at Denver's reuse demonstration plant. Future studies will include cost evaluations and the identification of organic by-products, as well as the analysis of additional pathogenic organisms such as *Giardia*, *Entamoeba*, *Salmonella*, *Campylobacter*, *Shigella*, and enteric viruses. The results of these studies, along with continued monitoring for the various organisms discussed in this article, will substantiate the proposition that water reclaimed from secondary wastewater effluent can satisfy the highest standards.

The generation of ClO_2 is highly sensitive to several factors, including Cl_2 concentration, NaClO_2 concentration, pH, mixing characteristics, and dilution effects. Monitoring methods that measure ClO_2 yield alone cannot predict the distribution of other chlorine species that may be present in the generator effluent. Therefore, to optimize ClO_2 generators, exacting analytical specification measurements must accompany

yield tests. Without these measurements, potentially harmful by-products may unknowingly be introduced into the water, thus negating a major benefit of ClO_2 usage, i.e., avoiding the formation of trihalomethanes, which are implicated as carcinogens.

Water treatment purveyors who may be contemplating conversion to ClO_2 should be aware that sophisticated chemical testing will be routinely required to verify that the generator is performing properly. This will be the case until new methods are developed for determining ClO_2 , ClO_2^- , ClO_3^- , and Cl_2 that are suitable for use by plant operators.

Acknowledgment

The authors thank Olin Water Services Company for supplying the generators described in this article and Brian Nelsen, Sanford Dee, and Anthony LaChance for their assistance in assembling and analyzing the data. They also thank the laboratory scientists and plant operations personnel.

Although the research described in this article has been funded wholly or in part by United States Environmental Protection Agency contract CS-806821 to the Denver Board of Water Commissioners, the article has not been subject to the agency's review and therefore does not necessarily reflect the views of the agency. No official endorsement should be inferred.

References

- LAUER, W.C. & WORK, S.W. The Denver Potable Water Reuse Project: Initial Plant Start-Up. *Proc. 1984 AWWA Ann. Conf.*
- LAUER, W.C.; ROGERS, S.E.; & RAY, J. M. The Current Status of Denver's Potable Water Reuse Project. *Jour. AWWA*, 77:7:52 (July 1985).
- WORK, S.W.; ARBER, R.P.; & LAUER, W.C. Transferring Concepts Into Designs—The Denver Reuse Project. *Proc. 1981 AWWA Ann. Conf.*
- OKUN, D.A. Reuse: Panacea or Pie in the Sky? *Jour. AWWA*, 77:7:26 (July 1985).
- CH2M Hill Inc. Conceptual Design Report—Potable Water Reuse Plant—Successive Use Program. Rept. to the Denver Bd. of Water Commissioners (1975).
- USEPA Protocol Development: Criteria and Standards for Potable Reuse and Feasible Alternatives. Rept. of Workshop Proc. Washington, D.C. (July 1980).
- National Inst. for Water Res. Manual for Water Renovation and Reclamation. Pretoria, South Africa (2nd ed., 1981).
- ROGERS, S.E. & LAUER, W.C. Disinfection for Potable Reuse. 58th Ann. WPCF Conf., Kansas City, Mo., Oct. 1985.
- LINSTEADT, K.D. & ROTHBERG, M.R. Potable Water Reuse. *Water Reuse* (E.J. Middlebrooks, editor). Ann Arbor Sci. Publ., Ann Arbor, Mich. (1982).
- ROGERS, S.E. & LAUER, W.C. Start-up and Operation of the Denver Potable Water Reuse Demonstration Plant. 57th Ann. WPCF Conf.
- GRABOW, W.O.K.; MIDDENDORF, I.G.; & BLASSON, N.C. Role of Chlorine Treatment in the Removal of Bacteria, Enteric Viruses, and Coliphages in a Wastewater Reclamation Plant. *Appl. Environ. Microbiol.*, 35:4:663 (Apr. 1978).
- WORK, S.W.; ROTHBERG, M.R.; & MILLER, K.J. Denver's Potable Reuse Project: Pathway to Public Acceptance. *Jour. AWWA*, 72:8:435 (Aug. 1980).
- ROTHBERG, M.R. ET AL. Demonstration of Potable Water Reuse Technology—The Denver Project. *Proc. AWWARF Water Reuse Sym. I* (1980).
- SCHMAUS, E. Ozone in Advanced Waste Treatment at the Denver Water Department Pilot Plant. Master's thesis, Univ. of Colorado, Boulder (1979).
- MILLER, G.W. ET AL. An Assessment of Ozone and Chlorine Dioxide Technologies for Treatment of Municipal Water Supplies. EPA-600/8-78-018 (Oct. 1978).
- BENARDE, M.A. ET AL. Efficiency of Chlorine Dioxide as a Bactericide. *Appl. Microbiol.*, 13:776 (1965).
- O'Brien and Gere Inc. Disinfection/Treatment of Combined Sewer Overflows. EPA-600-2-79-134 (Aug. 1979).
- TIFFT, E.C. ET AL. Enhancement of High Rate Disinfection by Sequential Addition of Chlorine and Chlorine Dioxide. *Jour. WPCF*, 49:1652 (1977).
- MILLER, G.W. ET AL. An Assessment of Ozone and Chlorine Dioxide Technologies for Treatment of Municipal Water Supplies. EPA-600/2-78-147. Cincinnati, Ohio (1978).
- LAUER, W.C. The Denver Potable Water Reuse Demonstration Project—Experimental Design. Rept. submitted to Carl Brunner, WERL, USEPA (Sept. 1985).
- AIETA, E.M.; ROBERTS, P.V.; & HERNANDEZ, M. Determination of Chlorine Dioxide, Chlorine, Chlorite, and Chlorate in Water. *Jour. AWWA*, 76:1:64 (Jan. 1984).
- MONSCVITZ, J.T. & REXING, D.J. Chlorine Dioxide Pilot Study. *AWWA Seminar on Water Disinfection with Ozone, Chloramines, or Chlorine Dioxide*, Atlanta, Ga., June 1980.
- MASSCHELEIN, W.J. Experience with Chlorine Dioxide in Brussels. *Jour. AWWA*, 77:1:73 (Jan. 1985).
- Standard Methods for the Examination of Water and Wastewater*. APHA, AWWA, and WPCF. Washington, D.C. (1985).



About the authors:
William C. Lauer is manager of the potable water reuse demonstration project at the Denver Water Department, 1600 W. 12th Ave., Denver, CO 80254, where he has also worked as a chemist and as assistant superintendent of water treatment. A graduate of the University of California at Irvine and of the University of Colorado at Boulder, Lauer is a member of AWWA and has had articles published in such journals as *JOURNAL AWWA* and *Journal WPCF*. Stephen R. Lohman is chief chemist at the Denver Water Department, and Stephen E. Rogers is supervisor of the reuse plant.